Catalytic Analysis. XVI : Microdetermination of Ruthenium with Ukena's Colorimeter

Catalytic Analysis. XVI Microdetermination of Ruthenium with Ukena's Colorimeter*

Takanobu SHIOKAWA

The Research Institute for Iron, Steel and Other Metals

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Synopsis

Applying the catalytic behaviour of ruthenium to the reaction between potassium chlorate and iodide, a microdetermination of ruthenium was carried out. By the relation between the time measured as the reaction velocity and the amount of ruthenium found experimentally, microamount of ruthenium was determinable with Ukena's colorimeter.

I. Introduction

Ruthenium has a catalytic behaviour on the reaction between potassium chlorate and iodide[1] as osmium[2] and vanadium[3] which had been applied, respectively, to the microdeterminations of them. Applying the behaviour of ruthenium, an attempt to determine the microquantities of ruthenium was made with Ukena's colorimeter as in the preceding papers.

II. Experimental results

1. Reagents and procedure

Potassium chlorate and iodide, and other reagents were all pure chemicals. Ruthenium chloride (Kahlbaum) was dissolved in a diluted hydrochloric acid and the concentration of ruthenium of the stock solution was 2 mg/ml, which was determined gravimetrically as usual, and it was diluted to a modarate concentration with water before it was used. Starch solution was 0.5% aqueous one containing no other reagent.

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* The 642nd report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Chemical Society of Japan, **71** (1950), 87.

(1) F. Feigl, *Qual. Anal. mit Hilfe von Tupfelreakitionen*, 2te Auf., 204 (1935).

(2) T. Shiokawa, Sci. Rep., RITU, A, **2** (1950), 290.

(3) T. Shoikawa, Ibid, **2** (1950), 613.

Potassium chlorate solution, sulfuric acid, potassium iodide solution, starch solution and rethenium solution were pipetted into a 50 ml Erlenmeyer flask and mixed well, and then the solution was transfered to a tube of the colorimeter. When the reagents were mixed, the time measurement was started, and the time required until the coloration of it matched with a standard colored solution described below, was measured to find the relation between the time and the amount of ruthenium, the catalyser, which should be available for the determination of the microquantities of it.

2. Standard colored solution

When the photometer was employed, the time required for a definite change of the transmittancy of the solution was measured as the reaction velocity, but if some standard solution having a stable coloration would be prepared, Ukena's colorimeter might be employed for the time measurement.

The reaction catalyzed with ruthenium would develop the deep blue color of iodine-starch. But a stable and definite coloration could not be obtained by iodine and starch, and, therefore, some other artificiall colored solution was looked for, which had a similar coloration and which was stable and reproducible. After some tests, a coloration of Congo Red in the HCl-KCl solution whose pH was 1.6 was found to be most suitable for the purpose. But, some precaution should be taken in the use of it, as shown in Table 1, because the stock solution of the dye is stable while a constant coloration in a such medium is kept for about two hours after the preparation. The coloration was measured with S_{57} (572 mμ) filter of Pulfrich's photometer, in which the solution consisted of 1.0 ml of 0.1% dye aqueous stock solution and 29.0 ml of HCl-KCl solution of pH 1.6. Therefore, the standard colored solution should be prepared with two stock solutions of 0.1% dye aqueous solution and HCl-KCl solution of pH 1.6, which must be used between 2~5 hours after the preparation.

Table 1. Extinctancy of Congo Red solution at pH 1.6.

Original Congo Red solution prepared ago (day)	Extinctancy measured after some hours						
	0	1	2	3	4	5	6(hours)
0	1.26	1.19	1.14	1.12	1.11	1.10	1.09
0	1.24	1.18	1.14	1.12	1.12	1.11	1.09
5	1.22	1.19	1.14	1.12	1.11	1.10	1.08
5	1.24	1.18	1.13	1.12	1.11	1.11	1.09

3. Concentration of potassium chlorate

The fact found experimentally that the catalytic behaviour of ruthenium was most sensitive in an excess of potassium iodide was studied in detail.

Various amounts of 4% potassium chlorate were used against 2 ml of 8% potassium iodide together with 2.5 ml of 5 N sulfuric acid and 1.0 ml of 0.5% starch solution in the 15 ml total solution, and the time measurements were all made at 20°C to find the most suitable concentration of it. The results obtained show, as tabulated in Table 2, that the higher concentration makes the reaction more rapid either in presence or absence of ruthenium. The large value in blank is not fitted for the purpose, so it may be said that the suitable amount of it to be used in the 15 ml total solution is about 0.5 ml.

Table 2. Concentration of potassium chlorate

4% $KClO_3$ used (ml)	Time measured with 80γ Ru (Mean of twice) (min)	Time measured without Ru (Mean of twice) (min)
0.3	8.45	above 70
0.5	5.93	67.0
0.7	4.86	56.5
1.0	2.70	38.5
1.5	1.62	27.3

4. Concentration of sulfuric acid

Sulfuric acid concentration has also an important effect on the reaction velocity as in the microdeterminations of osmium and vanadium cited above.

Various amounts of 5 N sulfuric acid were used in the 15 ml total solution together with 0.5 ml of 4% potassium chlorate, 2.0 ml of 8% potassium iodide and 1.0 ml of 0.5% starch solution, and the time measurements were all made at 20°C. The results obtained are given in Table 3, which shows that the suitable amount to be used is about 2.5 ml.

Table 3. Concentration of sulfuric acid

5N H_2SO_4 used (ml)	Time measured with 80γ Ru (Mean of twice) (min)	Time measured without Ru (Mean of twice) (min)
1.0	10.13	——
1.5	8.53	Above 70
2.0	7.19	69
2.5	6.25	71
3.0	5.76	59.5
3.5	5.10	55
4.0	4.80	49

5. Amount of ruthenium and reaction velocity

Under most suitable condition, which was found in the preliminary experiments described above, the time measurements were made with various amounts of ruthenium in order to find the relation between the time and the amount of

ruthenium.

Various amounts of ruthenium were added, respectively, in the 15 ml total solution against 0.5 ml of 4% potassium chlorate, 2.5 ml of 5 N sulfuric acid, 2.0 ml of 8% potassium iodide and 1.0 ml of 0.5% starch solution, and the time measurements were made at 25° and 35°C. As illustrated in Fig. 1, if the reciprocals of the time measured are plotted against the amount of ruthenium, linear relations are found at 25° and 35°C, respectively, which render it possible to determine 15~80 γ of ruthenium by the time measurement under the same condition.

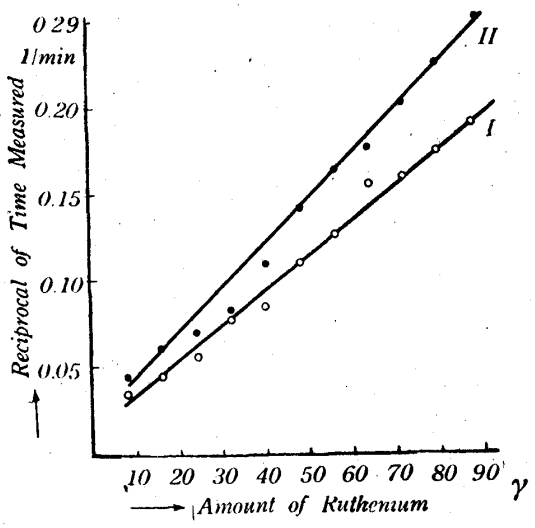

Fig. 1 Amount of ruthenium and reaction velocity.
I: At 25°C
II: At 35°C

6. Effects of diverse ions

Adding various amounts of diverse ions to the solution which contained a definite amount of ruthenium, their effects were tested. A solution of ammonium molybdate, sodium tungstate, chromium sulfate, mercuric chloride, manganese chloride, zinc chloride, nickel chloride or potassium nitrate was added, respectively, against 0.5 ml of 4% potassium chlorate, 2.5 ml of 5 N sulfuric acid, 2 ml of 8% potassium iodide, 1.0 ml of 0.5% starch solution and 40 or 80 γ of ruthenium in the 15 ml final solution and the time measurements were made at 25°C. The results obtained show, as tabulated in Table 4, that tungsten, manganese and zinc have

Table 4. Effects of diverse ions

Ion added (mg)	Time measured with 40γ Ru (Mean of twice) (min)				Time measured with 80γ Ru (Mean of twice) (min)			
	Mo^{6+}	W^{6+}	Cr^{3+}	Hg^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}	NO_3^-
0	15.51	15.70	11.05	13.56	8.72	5.38	4.95	6.33
2	15.74	15.52	11.20	12.15	8.80	5.20	4.14	6.88
4	14.88	15.92	11.29	11.39	8.32	5.93	3.21	7.05
6	14.56	15.15	12.35	10.93	8.72	5.66	2.65	7.92
8	12.50	15.25	12.40	10.43	8.32	5.31	2.53	8.00
10	13.86	15.40	12.40	10.19	8.84	5.42	2.60	7.15

no effects even in the presence of 10 mg of them, and chromium, molybdenum, mercury, nickel and nitrate have some interference. But, if those interfering ions were present in a definite amount in the solution containing various amounts of

ruthenium, the above described relation between the reciprocals of the time measured and the amount of ruthenium, was just the same as in the absence. In Fig. 2, the results in the presence of 3 mg of nickel or 10 mg of nitrate, are illustrated as a sample of them, which shows that the determination may be possible under such a condition.

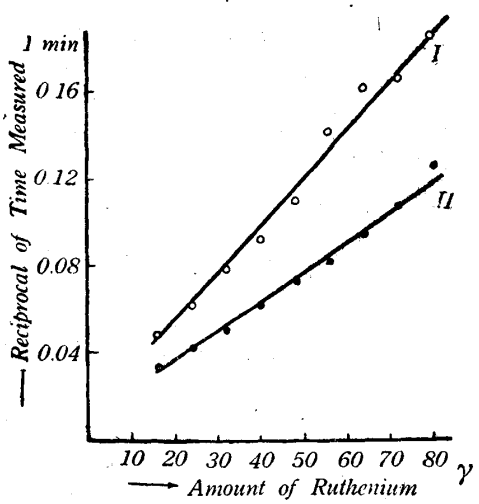

Fig. 2 Amount of ruthenium and reaction velocity in the presence of some diverse ion.
I: Ni^{3+} 3mg
II: NO_3^- 10mg

Summary

(1) Applying a catalytic behaviour on the reaction between potassium chlorate and iodide in a sulfuric acid solution, the microdetermination of ruthenium was studied with Ukena's colorimeter by the use of standard colored solution.

(2) The suitable standard colored solution and the suitable concentration of reagents were discussed, and under the definite condition, it was found that the reciprocals of the time required for the reaction were linear against the amount of ruthenium.

(3) The relations between the time and the amount of ruthenium rendered it possible to determine 15~80 γ of ruthenium by the time measurement under the same condition.

(4) Influences of some diverse ions on the determination were examined.

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